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**RPPR Final Report**  
as of 12-Apr-2018

Agency Code:

Proposal Number: 64880EG

**Agreement Number: W911NF-14-1-0250**

**INVESTIGATOR(S):**

**Name:** Michelle Lacchia Pantoya Ph.D.

**Email:** michelle.pantoya@ttu.edu

**Phone Number:** 8068343733

**Principal:** Y

Organization: **Texas Technical University**

Address: Box 41035, Lubbock, TX 794091035

Country: USA

DUNS Number: 041367053

EIN: 756002622

**Report Date:** 01-Jan-2016

Date Received: 09-Apr-2018

**Final Report** for Period Beginning 01-Jun-2014 and Ending 30-Nov-2017

**Title:** Characterizing Ignition, Combustion, and Energy Transfer from Composite Energetic Materials

**Begin Performance Period:** 01-Jun-2014

**End Performance Period:** 30-Nov-2017

**Report Term:** 0-Other

Submitted By: Michelle Pantoya

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**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 6

**STEM Participants:** 15

**Major Goals:** This project examines surface reactions of aluminum particles with various halogenated oxidizers and ignition and combustion properties affected by these surface reactions. The main goal is to enhance aluminum reactivity through understanding surface exothermic kinetics that facilitate combustion. These surface reactions catalyze overall reactivity and are triggered by a halogen based oxidizer, such as fluoropolymers, iodine or chlorine species. The objective is to understand the reaction kinetics of halogens with the alumina passivation shell surrounding aluminum particles, then use this understanding to design formulations that show greater reactivity. Our focus is on three areas of research including: (1) developing mechanistic understanding of reaction pathways that promote surface reactions; (2) analyzing and modeling Al combustion for ignition and energy propagation; and, (3) synthesizing and characterizing novel formulations that capitalize on the surface reactions.

Specific research questions: (1) How does surface chemistry affect oxidation, chemical energy generation and reaction propagation; (2) What reaction pathways are needed to promote the surface reactions; (3) How can the alumina surface be manipulated to enhance surface reactions; (4) What reaction kinetics accelerate oxidation rates and how can those kinetics be exploited to synthesize new formulations; (5) What controlling mechanisms and modes of energy transport are dominant and how do those mechanisms vary with oxidizer.

**Accomplishments:** See Attached

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**Training Opportunities:** Under the guidance and supervision of the PI (Dr. Michelle Pantoya), students design and conduct experiments as a team. For each avenue of work, one person takes the lead and is primarily responsible for the project; this in turn gives each student first authorship position on a paper. Also, students visited ARL (Aberdeen) with the PI every year of this project and actively collaborate with Staff Scientists at ARL including, Drs. Jennifer Gottfried, Chi-Chin Wu, Steven Dean, and Kevin McNesby as evidenced by their co-authorship on papers. Also, students from our group have been selected for summer internship experiences at ARL (i.e., Ms. Kelsea Miller for summer 2018 with Dr. Chi-Chin Wu as her mentor). The exchange of students facilitates further collaborative experiments.

Also, graduate and undergraduate students are trained on the safe handling of energetic materials as well as the proper use of our advanced combustion diagnostics and equipment and follow safe operating procedures while conducting experiments. Sometimes this includes professional development training at other institutions. For example, a high speed diagnostic workshop was held at Colorado School of Mines in October, 2017 and two students, Lee Campbell and Ryan Bratton participated in that training, along with several from ARL Aberdeen Proving Ground. The workshop also solidified further collaborations specific to visualization of high speed reactions.

By working on this project students learn how concepts taught in the classroom relate to real world applications and gain a hands-on approach to the use of modern technological equipment. An essential element of our internal training plans is to give students insight into practical applications of combustion theories and allow them to explore career possibilities at military labs that utilize their developing skill set for military relevant applications.

To be clear, all research activities involve participation of students such that by designing experiments, students establish a link between the theoretical concepts they learn in the classroom and the practical, bottom-line methods used to perform research. We have established a strong mentoring program within the Energetic Materials Combustion Laboratory such that students feel comfortable asking questions at all times and have guidance and instruction from a faculty and/or student mentor. It is our policy that all new students spend at least 6 months being mentored by a more experienced student before they assume their own project. In fact, our safety practices have been published in Propellants, Explosives, Pyrotechnics as a guideline for other researchers handling energetic materials. Integrating the advanced diagnostic equipment proposed here also helps foster graduate student mentoring and facilitate our goal of integrating state of the art research into the learning environment.

We also strongly promote collaboration with other academics from other universities and national and military lab scientists as well as industry such that students practice communicating and working with outside organizations to achieve common project goals. In fact, almost every research project we pursue links a student from our group with an individual at ARL, or other outside organization as a collaborator.

Over the course of this project more than 20 students worked on different aspects of this project and developed skills essential for their success as energetic material scientists of the future.

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**Results Dissemination:** The scientific results of this project were presented in top ranking scientific journals covering a broad spectrum of scientific disciplines including general science (Scientific Reports), physical chemistry (e.g., Journal of Physical Chemistry, Physical Chemistry Chemical Physics), metallurgy and material science (Journal of Materials Chemistry, Journal of Materials Science, Acta Materialia), physics (Journal of Applied Physics, Physical Reviews E), math (Applied Mathematical Modelling) and combustion (Combustion and Flame).

Further, the results were disseminated to multi-disciplinary national and international conferences covering material science (Material Research Society, MRS), physics (American Physical Society, APS), thermal analysis (North American Thermal Analysis Society, NATAS) and chemistry (American Chemical Society, ACS) meetings. An interdisciplinary review in a Progress in Energy and Combustion Science is also pending.

Graduate students promoting this research at conferences, review meetings, and workshops that graduated are now all employed in the US and continue to work in the field of energetic materials. These individuals continue to disseminate results of this work through and develop new ideas from this work that are the premise of their current work. These individuals include:

1. Dr. Billy Clark, R&D Director, BiSN, Houston, Texas
2. Dr. Keerti Kappagantula, Assistant Professor, University of Ohio
3. Dr. Jena McCollum, Assistant Professor, University of Colorado, Colorado Springs
4. Dr. Kelsea Meeks, Staff Scientist, Sandia National Laboratory, New Mexico
5. Dr. Richa Padhye, Staff Material Scientist, Intel R&D, Oregon
6. Dr. Dylan Smith, Post Doc, Eglin Air Force Base, Florida
7. Mr. Ethan Zepper, Staff Scientist, Sandia National Laboratory, New Mexico

The specific scientific results will provide a broader context for the following key contributions:

- ? New understanding of the synthesis and reactivity of aluminum particles and their tailored properties that exhibit heightened reactivity. New understandings that purposefully enable greater Al reactive productivity in a variety of energetic material environments.
- ? New models, subroutines, and simulation results that will bring our modeling capabilities in surface chemistry of energetic materials at the next level and extend our understanding and capabilities to control corresponding fundamental reaction processes.
- ? Novel experimental methodologies for studying energy release that includes (1) new processing techniques involving surface chemistry manipulation within a core-shell particle towards higher reactivity; (2) novel in-situ diagnostics to resolve surface kinetic pathways that promote reactivity within particles; and, (3) analysis of various combustion conditions to resolve fundamental reaction mechanisms.
- ? Novel technologies for synthesis of aluminum particles with tunable and optimized properties.
- ? Fundamental data on reaction of aluminum particles.

**Honors and Awards:** 1. Discovery Channel Daily Planet "Green Ammunition" featuring ARO supported research - aired Sept. 2014

2. Dr. Michelle the Engineer - PBS Kids segments introducing engineering to young children - aired regularly in 2014-Present.

3. YWCA Women in Excellence Award (Science) 2015.

4. Outstanding Research Award, Texas Tech University 2015, 2016.

5. Dr. Pantoya was honored with several invited speaker presentations and key note speech invitations throughout the year including the Gordon Conference on Energetic Materials and the ACS Fluoropolymer meeting.

6. M. Pantoya received the Texas Tech Alumni Association Bernie E. Rushing Faculty Distinguished Research Award in 2017.

7. Dr. Pantoya was re-appointed as the J. W. Wright Regents Endowed Chair Professor in 2017.

**Protocol Activity Status:**

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**Technology Transfer:** Regarding technology transfer, we have had several interactions with scientists from DoD laboratories and industry that are still ongoing and related to this project. These are highlighted as follows:

- Drs. Brian Fuchs and Philip Stiel (ARL) – TTU synthesized ~ 20 grams of AIH-AI was synthesized and sent it to Philip Stiel for measurements of parameters needed for their detonation simulation modeling. Also, Brian visited TTU in February, 2017, to give a seminar. He has hired a student from my group, Mr. Loudon (Lee) Campbell to work on aluminized propellants processed using additive manufacturing techniques at Picatinny Arsenal summer 2018.
- Drs. Stephen Howard, Richard Beyer (ARL) – We have been working on developing a high UV emission formulation that can be transferred to Dr. Beyer's ARL group. Dr. Stephen Howard visited TTU in April 2017 to give a seminar. We are planning for Dr. Beyer to visit in 2018 and we hope to collaborate with him further on gun propellants.
- Drs. Jennifer Gottfried and Steven Dean (ARL) – TTU synthesized ~ 5 grams of various AIH-AI formulations sent to Jennifer for LASEM analysis. Her preliminary results show that some formulations of AIH-AI react at time scales relevant to a detonation event and overall improve the detonation velocity of TNT. Our journal publication reporting these results is pending publication in Scientific Reports and our continued collaboration is ongoing. She also visited TTU to give a seminar in October 2016. Dr. Steven Dean and I wrote a white paper in response to a DTRA solicitation. The proposal was to establish diagnostics to quantify fragmentation from impacting reactive materials. The proposal was declined. We are now working together on designing experiments to study impact ignition of AI-AIH samples that would be used in his laser driven flier plate apparatus at ARL.
- Dr. Jessie Sabatini (ARL) – Jessie visited TTU to give a seminar in January 2017 and provided instruction to our group on how to nitrate some formulations. Our collaboration will characterize the reactivity of nitrated plasticizer that he synthesizes. His formulations would be sent to us as inert that we then nitrate. Specific formulation: bis-isoxazole-bis-methylene dinitrate (BIDN).
- Dr. Chi-Chin WU (ARL) – Chi-Chin is using TEM to analyze our AI and AIH-AI particles laying the foundation for continued work using plasma surface engineering to alter surface properties of the AI particles. We wrote an ARL external collaboration initiative (ECI) proposal together to help support our plans that was funded. This grant will provide support for a student from our group to work with Dr. Chi-Chin Wu during summer 2018 at ARL.
- Dr. Berry Homan and Kevin McNesby – Kevin has been working with us to develop a high speed temperature measurement system based on multi-color pyrometry. The diagnostic will complement our high speed IR camera by expanding the temperature range of our measurements over time scales relevant to fast reacting materials.
- Dr. Ron Heaps (Idaho National Lab) – Ron is developing a model using MOOSE software to predict energy propagation behavior in thermites. To complement his efforts, our group is performing a series of flame speed experiments using diagnostics we developed through ARO support that will help validate the model. The model has the potential for being a supplement to already established CHEETAH type software used for thermodynamic predictions that would extend analysis towards combustion properties like deflagration velocity. Ron visited TTU to give a seminar in February 2017.
- Dr. Mehmet Kesmez & Mr. Jeff Parkey (Lynnntech, Inc., College Station, TX) – Mehmet and Jeff are synthetic chemists that developed efficient methods for synthesizing pure iodine oxides ( $I_2O_5$ ,  $HIO_3$ ). They supplied us with many iodate samples that we used to eventually develop the AI-AIH formulations.
- Dr. John Granier (EMPI, Inc., Austin, TX) – John designed and built a laboratory scale high velocity impact tester and installed and trained students on its safety and use in our lab. This will enable studies of impact ignition at high velocities (~4000 ft/s).
- Dr. Christopher Junk (DuPont) – Supplies us with small quantities of new and unique fluoropolymers that we use for our ARO project to analyze surface chemistry.
- Drs. Carol Korzenowski, Daniel Unruh and Adelia Aquino (TTU), Daniel Tunega (Univ. Nat. Resources and Life Sci., Vienna, Austria) - Carol is a spectroscopist and aids in our design of surface chemistry experiments and FTIR analysis; Daniel Unruh is a XRD technician that has helped identify AIH; Adelia and Daniel Tunega perform density functional theory (DFT) simulations that complement our surface chemistry experiments. Daniel Tunega visited

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TTU to give a seminar in March 2017.

**PARTICIPANTS:**

**Participant Type:** PD/PI

**Participant:** Michelle Pantoya

**Person Months Worked:** 2.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Faculty

**Participant:** Adelia Aquino

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Technician

**Participant:** Julio Warzywoda

**Person Months Worked:** 2.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Michael Bello

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Billy Clark

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Jena Mccollum

**Person Months Worked:** 12.00

**Funding Support:**

Project Contribution:

International Collaboration:

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International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)  
**Participant:** Kelsey Meeks  
**Person Months Worked:** 6.00 **Funding Support:**  
Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)  
**Participant:** Richa Padhye  
**Person Months Worked:** 12.00 **Funding Support:**  
Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)  
**Participant:** Dylan Smith  
**Person Months Worked:** 12.00 **Funding Support:**  
Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)  
**Participant:** Evan Vargas  
**Person Months Worked:** 4.00 **Funding Support:**  
Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)  
**Participant:** Ethan Zepper  
**Person Months Worked:** 12.00 **Funding Support:**  
Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)  
**Participant:** Kevin Hill  
**Person Months Worked:** 10.00 **Funding Support:**  
Project Contribution:

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International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Kevin Hill

**Person Months Worked:** 10.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Connor Woodruff

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Ryan Bratton

**Person Months Worked:** 12.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Loudon Campbell

**Person Months Worked:** 12.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Undergraduate Student

**Participant:** Colt Cagle

**Person Months Worked:** 12.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Staff Scientist (doctoral level)

**Participant:** Nobumichi Tamura

**Person Months Worked:** 1.00

**Funding Support:**



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Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Staff Scientist (doctoral level)

**Participant:** John Tencer

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Faculty

**Participant:** Keerti Kappagantula

**Person Months Worked:** 2.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Faculty

**Participant:** Gordon Christopher

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Technician

**Participant:** Daniel Unruh

**Person Months Worked:** 2.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Staff Scientist (doctoral level)

**Participant:** Mehmet Kesmez

**Person Months Worked:** 2.00

**Funding Support:**

Project Contribution:  
International Collaboration:  
International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Faculty

**Participant:** Daniel Tunega

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**Person Months Worked:** 2.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Staff Scientist (doctoral level)

**Participant:** Michael Daniels

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Faculty

**Participant:** Jordan Berg

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Faculty

**Participant:** Micha Green

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Undergraduate Student

**Participant:** Jose Cano

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**CONFERENCE PAPERS:**

**RPPR Final Report**  
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**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** Central States Section of the Combustion Institute  
Date Received: 23-Aug-2016 Conference Date: 21-Nov-2014 Date Published: 21-Nov-2014  
Conference Location: Tulsa, OK  
**Paper Title:** Catalyzing Aluminum Particle Reactivity Using Surface Exothermic Chemistry  
**Authors:** Richa Padhye, Michelle L Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** Gordon Research Conference on Energetic Materials  
Date Received: 23-Aug-2016 Conference Date: 02-Jun-2016 Date Published: 23-Aug-2016  
Conference Location: Stowe, Vermont  
**Paper Title:** Enhancing Aluminum Reactivity  
**Authors:** Michelle L. Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** International Conference on Metallurgical Coatings and Thin Films  
Date Received: 23-Aug-2016 Conference Date: 09-May-2016 Date Published: 16-May-2016  
Conference Location: San Diego, CA  
**Paper Title:** Combustion characterization of nano particle reactive materials suspended in polymer binders for use in additive manufacturing  
**Authors:** Jennifer Cox, Billy Clark, Michelle Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** Schlumberger  
Date Received: 23-Aug-2016 Conference Date: 17-Feb-2016 Date Published: 17-Feb-2016  
Conference Location: Houston, TX  
**Paper Title:** Aluminum Combustion: Resolving Fundamental Parameters Promoting Reactivity  
**Authors:** Michelle L. Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** 14th Pacific Polymer Conference  
Date Received: 23-Aug-2016 Conference Date: 09-Dec-2015 Date Published: 14-Dec-2015  
Conference Location: Kauai, Hawaii  
**Paper Title:** Aluminum Fluoropolymer Combustion  
**Authors:** Jena McCollum, Michelle L. Pantoya, Scott Iacono  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** JANNAF  
Date Received: 23-Aug-2016 Conference Date: 15-Dec-2015 Date Published: 15-Dec-2015  
Conference Location: Salt Lake City, UT  
**Paper Title:** Teaching Energetic Material Safety  
**Authors:** Michelle L. Pantoya  
Acknowledged Federal Support: **Y**

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**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** National Conference on Energetic Materials and Additive Manufacturing  
Date Received: 23-Aug-2016 Conference Date: 12-Oct-2015 Date Published: 15-Oct-2015  
Conference Location: Lubbock, TX  
**Paper Title:** First Steps Toward Developing Additive Manufacturing of Energetic Materials  
**Authors:** Michelle L. Pantoya  
Acknowledged Federal Support: Y

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** JANNAF – Join Army, Navy, NASA, Air Force 9th Liquid Propulsion Joint Subcommittee Meeting  
Date Received: 04-Aug-2017 Conference Date: 05-Dec-2016 Date Published: 05-Dec-2016  
Conference Location: Phoenix, Arizona  
**Paper Title:** Additive Manufacturing of Mock Energetics  
**Authors:** Loudon Lee Campbell, Michael Sweeney, Gordon Christopher, Michelle Pantoya,  
Acknowledged Federal Support: Y

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** The Behavior, Fabrication and Promise of Intentionally Structured Energetic Materials  
Date Received: 04-Aug-2017 Conference Date: 10-Jan-2017 Date Published: 10-Jan-2017  
Conference Location: Santa Fe, NM  
**Paper Title:** Additive Manufacturing of Mock Energetics (Poster)  
**Authors:** L Campbell, M Sweeney, G Christopher, M Pantoya,  
Acknowledged Federal Support: Y

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** North American Thermal Analysis Society, International Conference for thermal analysis and calorimetry  
Date Received: 04-Aug-2017 Conference Date: 14-Aug-2016 Date Published:  
Conference Location: Orlando, FL  
**Paper Title:** The Influence of Environmental Processing Conditions on the Reactivity of Aluminum with Various Oxidizing Agents  
**Authors:** Richa Padhye, Michelle Pantoya  
Acknowledged Federal Support: Y

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** American Institute of Chemical Engineers Annual Meeting  
Date Received: 04-Aug-2017 Conference Date: 14-Nov-2016 Date Published:  
Conference Location: San Francisco, CA  
**Paper Title:** Aluminum Surface Reactivity  
**Authors:** Richa Padhye, Michelle Pantoya  
Acknowledged Federal Support: Y

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** American Physical Society  
Date Received: 04-Aug-2017 Conference Date: 13-Mar-2017 Date Published:  
Conference Location: New Orleans, LA  
**Paper Title:** Engineering surface properties of reactive materials  
**Authors:** Richa Padhye, Michelle Pantoya  
Acknowledged Federal Support: Y

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**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** European Materials Research Society Spring Meeting  
Date Received: 04-Aug-2017 Conference Date: 13-Mar-2017 Date Published:  
Conference Location: Strasbourg, France  
**Paper Title:** Engineering surface properties of reactive materials  
**Authors:** Richa Padhye, Michelle Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** 10th U.S. National Combustion Institute Meeting  
Date Received: 04-Aug-2017 Conference Date: 24-Apr-2017 Date Published:  
Conference Location: College Park, MD  
**Paper Title:** A Closer Look at Determining Flame Speeds with Imaging Diagnostics  
**Authors:** Ryan Bratton, Michelle Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** International Conference of Metallurgical Coatings and Thin Films  
Date Received: 07-Aug-2017 Conference Date: 24-Apr-2017 Date Published:  
Conference Location: San Diego, CA  
**Paper Title:** A Closer Look at Determining Flame Speeds with Imaging Diagnostics  
**Authors:** Connor Woodruff, Ryan Bratton, Michelle Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** 10th US US National Combustion Institute Meeting  
Date Received: 07-Aug-2017 Conference Date: 24-Apr-2017 Date Published:  
Conference Location: College Park, MD  
**Paper Title:** Combustion Behavior of Surface Functionalized Aluminum Particles Dispersed in Kerosene  
**Authors:** Michael Bello, Dylan Smith, Michelle Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** American Physical Society  
Date Received: 08-Aug-2017 Conference Date: 15-Mar-2017 Date Published:  
Conference Location: New Orleans, Louisiana  
**Paper Title:** Oxoacid Synthesis of Aluminum Energetic Materials: Aluminum Iodate Hexahydrate  
**Authors:** Dylan Smith, Daniel Unruh, Michelle L. Pantoya  
Acknowledged Federal Support: **Y**

**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** The behavior, fabrication, and promise of intentionally structured energetic materials, Los Alamos National Laboratory Sponsored Workshop  
Date Received: 08-Aug-2017 Conference Date: 10-Jan-2017 Date Published:  
Conference Location: Santa Fe, NM  
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**Title:** Replacing the Al<sub>2</sub>O<sub>3</sub> Passivation Shell on Aluminum Nano-Particles with an Energetic Salt: Aluminum Iodate Hexahydrate (AIH)

**Authors:** Dylan K. Smith

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**Authors:** Richa Padhye

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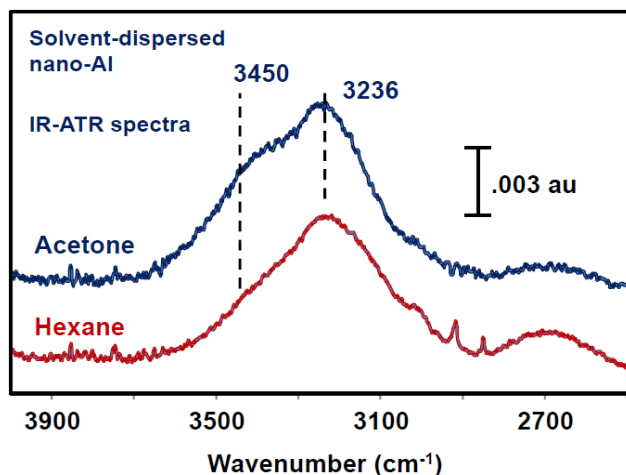
# Characterizing Ignition, Combustion, and Energy Transfer from Composite Energetic Materials

*Michelle Pantoya, Texas Tech University*

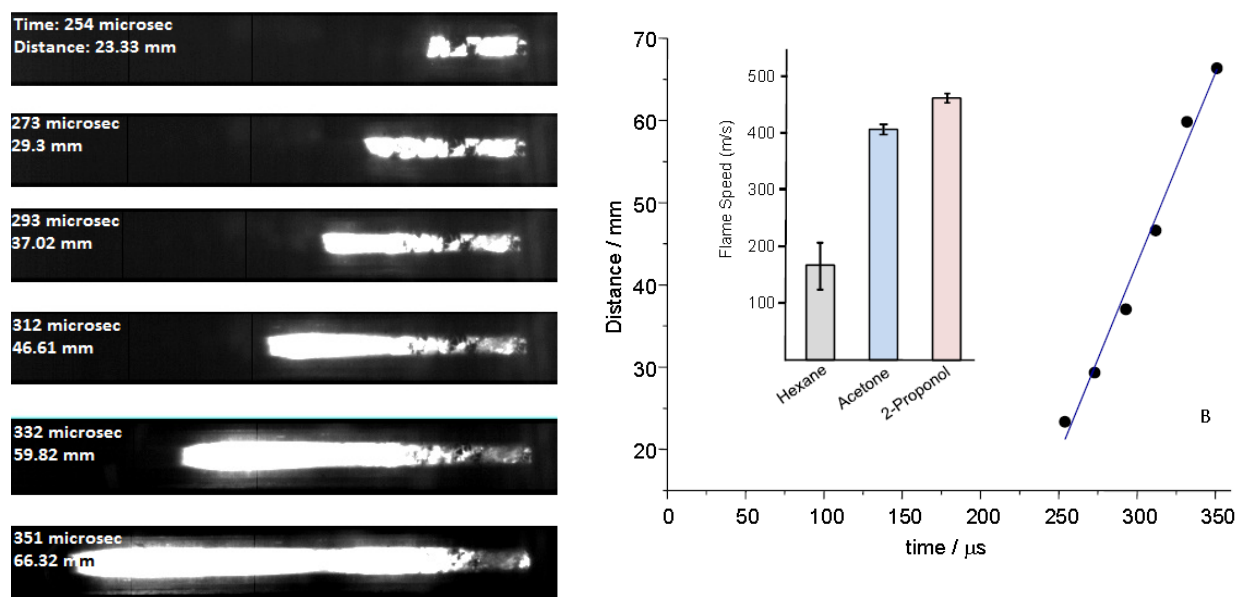
## Accomplished under Goals

Below summarizes our accomplishments towards understanding how surface chemistry affects oxidation and then towards controlling metal particle reaction mechanisms promoting combustion that will enhance energy release of the stored chemical energy within metal fuel particles at time scale relevant to detonations and deflagrations.

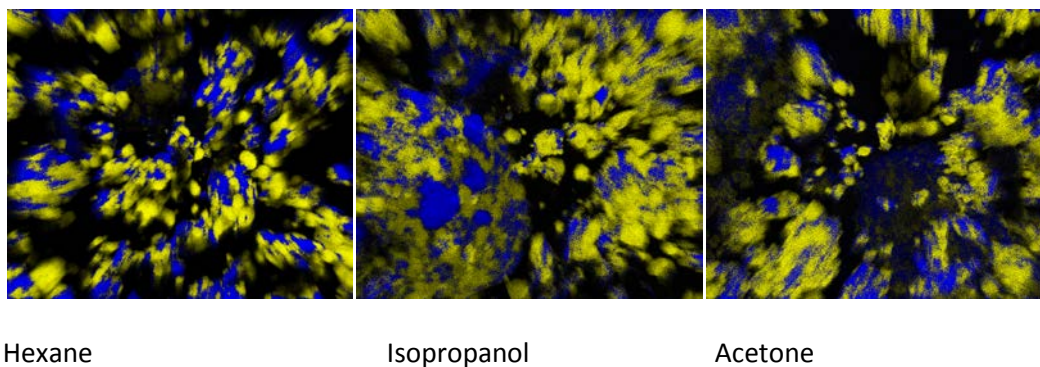
We are identifying key reaction pathways that promote the pre-ignition reaction (PIR). The PIR is reaction between the alumina shell surface and a halogen (e.g., F, I, Cl) and promotes overall Al reactivity. We investigated the literature on alumina catalysis and learned that hydroxyl bonding, inherent on alumina, may be a key indicator in the onset and magnitude of the PIR. Many have shown that alumina acts as a catalyst because of  $\text{-OH}$  bonds and certain  $\text{-OH}$  bonding configurations tend to promote catalytic activity. We have taken this understanding to Al reactivity. We treated alumina and aluminum powders in various solvents that differ in their polarity and differ in their water immiscibility. The treatment produced controlled growth of hydroxyl concentrations on the alumina surface. We found that Al particles treated in polar solvents retained liquid-like water capable of hydrogen bonding with sites on the  $\text{Al}_2\text{O}_3$  lattice (**Fig. 1**). Our FTIR analysis resulted in a sum frequency vibrational spectra shoulder peak at  $3450\text{ cm}^{-1}$ . This peak was not observed for hexane treated samples that displaced liquid like water from the  $\text{Al}_2\text{O}_3$  shell, leaving the hydration layer within the shell dominated by more strongly bound structured water (**Fig. 1**). The presence of the liquid-like water correlates with earlier onset and greater magnitude of the PIR when combined with polytetrafluoroethylene (PTFE). Promoting this PIR also correlates with increasing the flame speed and reactivity of Al. Specifically, treatment in polar solvents results in flame speeds on the order of 406-460 m/s while the non-polar hexane treatment produces 165 m/s (**Fig. 2**). The different treatments did NOT affect reactivity when Al was combined with a metallic oxides such as  $\text{CuO}$  or  $\text{MoO}_3$ . Physical mixing homogeneity was observed consistent among all solvent treated samples (**Fig. 3**). This is the first indication that specific hydroxyl configurations and concentrations promote  $\text{Al}_2\text{O}_3$  catalysis and Al reactivity.



**Figure 1.** FTIR spectra for Al nano-powder treated in acetone and hexane. Shoulder at  $3450\text{ cm}^{-1}$  represents liquid like water and broad peak at  $3236\text{ cm}^{-1}$  represents crystalline water. When Al particles exhibit shoulder peak at  $3450\text{ cm}^{-1}$ , their reactivity is increased. Polar solvents promote the growth of liquid



**Figure 2.** (A) Representative still frame images showing flame propagation in a nano-Al/PTFE mixture following treatment in acetone. The numbers indicate time in  $\mu\text{s}$ . (B) Plot of the average flame speed for Al + PTFE mixtures following treatment in the indicated solvents. The error bars give the 95 % confidence limits based on three repetitive measurements.



**Figure 3.** Colored maps from SEM with EDAX showing Al (yellow) and F (blue) distribution within Al + PTFE mixtures treated in the solvents indicated.



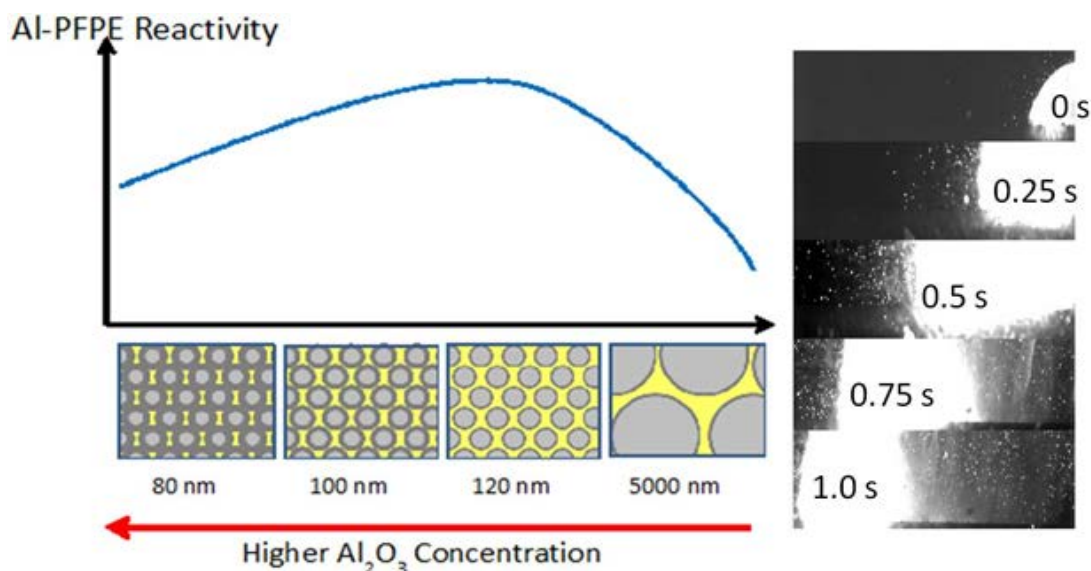
Molecular dynamic simulations predict –OH bonding to the  $\text{Al}_2\text{O}_3$  surface (**Fig. 4**). We solicited collaboration with molecular dynamic modelers that perform *ab initio* calculations using density functional theory (DFT) on the –OH configurations to alumina and to alumina treated in acetone to represent a hydrated surface. The results from the simulations show the hydration effect of the polar environment on the atomic distances as well as on the atomic charges. The O-H and  $\text{Al}_\text{t}$ -O distances are longer in the polar environment in comparison to the isolated state whereas the  $\text{Al}_\text{o}$ -O distances become shorter upon the solvent effect. Bonding variations will impact the chemical stability of the lattice.

We have also examined Al coated with highly viscous perfluoropolyether (PFPE) purposefully to promote a PIR and catalyze further reaction. Two projects were pursued. The first examined fundamentally Al- PFPE blends with varying Al particle sizes (80 -5500 nm in diameter). The results showed that combustion is highly dependent on the  $\text{Al}_2\text{O}_3$  exposed surface area that catalyzes PFPE decomposition (**Fig. 5**). High specific surface area associated with nano-Al particles promotes  $\text{AlF}_3$  formation via exothermic surface reaction identified as

the PIR. This reaction promotes the decomposition of PFPE (as seen by higher HF gas evolution in the QMS), and provides greater overall calorific output for diffusive energy propagation, as seen in the higher rates of energy propagation for nano-Al-PFPE blends. Activation energy was also measured and found to inversely correlate with flame speed indicating that reaction kinetics also play a dominant role in improving combustion performance. These results provide a new direction for catalyzing Al particles towards greater reactivity: by including a fluorinated oligomer to exploit exothermic surface reactions contributing toward overall energy generation. These results also introduce new opportunities for Al inclusion in applications such as fuel cells, batteries, as well as green and sustainable materials development.

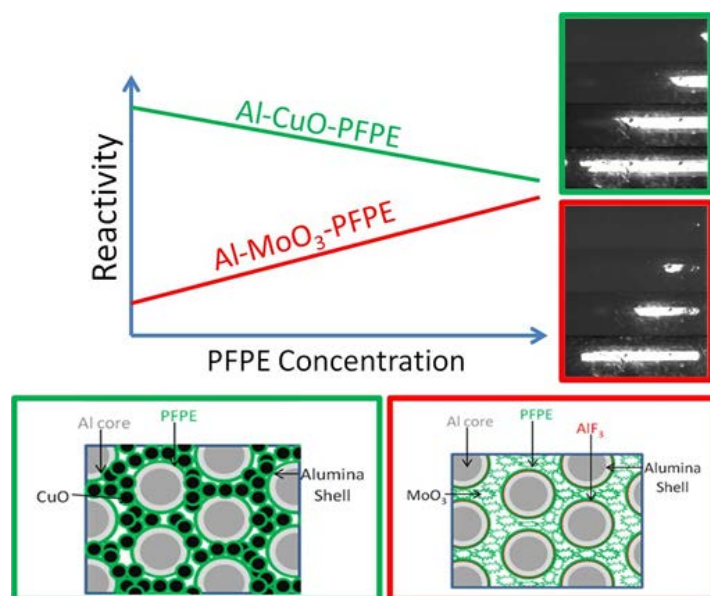
Site	O-H		$\text{Al}_\text{t}$ -O		$\text{Al}_\text{o}$ -O		Freq
	gas	acetone	gas	acetone	B-P	acetone	gas
I	0.978	0.988	-	-	1.799	1.794	3668
II	0.996	1.000	-	-	1.896	1.860	3639
III	0.975	0.980	-	-	1.973	1.960	3737
IV	0.979	0.989	1.743	1.746	-	-	3663
V	1.073	1.074	1.781	1.783	1.902	1.903	~3000

**Figure 4.** Table shows variation in bond distances for each structural site shown in the figure. Gas represents untreated alumina lattice and acetone represents treated alumina lattice. Frequency is in  $\text{cm}^{-1}$ . Overall, -OH bonding is ‘stretched’ upon treatment in acetone, likely making the surface –OH more unstable and lowering the activation energy required to induce the pre-ignition reaction. For the Al-O bonding, structures I and II are affected. Suggesting that these configurations may promote the PIR.



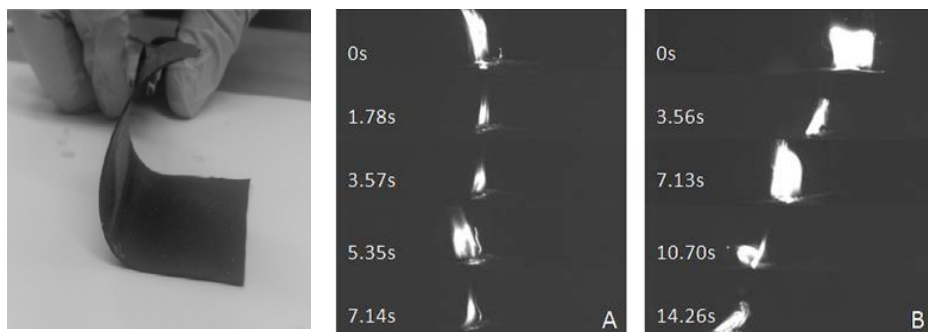
**Figure 5.** As Al particle diameter increases from 80 to 120 nm, the Al-PFPE blends exhibit an increase in flame speeds by 48% and a corresponding increase in surface exothermic reaction identified as a pre-ignition reaction (PIR) that promotes an increase in the calorific output of the main reaction. But, from 120 to 5500 nm Al-PFPE blends, flame speeds decrease by 93%. Fundamentally there is a balance between promoting PFPE decomposition (and F gas evolution) with greater surface area to volume ratio and increasing the PIR and main reaction exotherms toward optimizing reactivity. This balance is optimized for 120 nm Al powder.

We also investigated PFPE incorporated to activate Al reactivity in Al-CuO and Al-MoO<sub>3</sub>. Flame speeds, differential scanning calorimetry (DSC) and quadrupole mass spectrometry (QMS) were performed for varying percent PFPE blended with Al/MoO<sub>3</sub> or Al/CuO in order to examine reaction kinetics and combustion performance. X-ray photoelectron spectroscopy (XPS) was performed to identify product species. Results show that the performance of the thermite-PFPE blends is highly dependent on the bond dissociation energy of the metal oxide (**Fig. 6**). Fluorine-aluminum based surface exothermic chemistry with MoO<sub>3</sub> produce an increase in reactivity while the blends with CuO show a decline when increasing the PFPE loadings. We observed a decline in formation of AlF<sub>3</sub> in Al-CuO samples but an increase in AlF<sub>3</sub> formation in the Al-MoO<sub>3</sub> samples. The potential surface chemistry between Al<sub>2</sub>O<sub>3</sub> and F from PFPE is negated by competitive Al-O, but thermodynamically favorable formation from CuO with lower bond dissociation energy than F or the CF<sub>2</sub> radical. Basically, CuO is such a weak oxidizer (very low bond dissociation energy) that it will react with Al before F from decomposing PFPE. But, when using an oxidizer with a BDE similar to that of the C-C or C-F bond (i.e. MoO<sub>3</sub>), PFPE can promote reactivity via catalytic behavior of the alumina shell to help decompose PFPE more efficiently and improve the low temperature surface chemistry and overall reactivity.

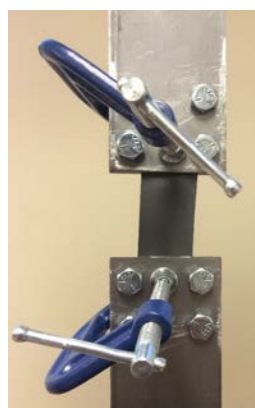


**Figure 6.** Results show that the performance of the thermite-PFPE blends is highly dependent on the bond dissociation energy of the metal oxide. Fluorine-aluminum based surface exothermic chemistry with  $\text{MoO}_3$  produce an increase in reactivity while the blends with  $\text{CuO}$  show a decline when increasing the PFPE loadings. These results provide new evidence that optimizing aluminum combustion can be achieved through activating exothermic Al surface chemistry.

Understanding the role of binders on Al combustion has led to the development of a new approach for synthesizing extrudable energetics. Film energetics are becoming increasingly popular because a variety of technologies are driving a need for localized energy generation in a stable, safe and flexible form. Aluminum (Al) and molybdenum trioxide ( $\text{MoO}_3$ ) composites were mixed into a silicon binder and extruded using a blade casting technique to form flexible free-standing films ideal for localized energy generation (**Fig. 7**). Since this material can be extruded onto a surface it is well suited to additive manufacturing applications. This study examines the influence of 0-35% by mass potassium perchlorate ( $\text{KClO}_4$ ) additive on the combustion behavior of these energetic films. Without  $\text{KClO}_4$  the film exhibits thermal instabilities that produce unsteady energy propagation upon reaction. Results show that the silicone binder participates as a fuel and reacts with  $\text{KClO}_4$  adding energy to the reaction and promoting propagation. No PIR was observed for the reaction between  $\text{KClO}_4$  and Al, implying that Cl may not catalyze Al reactivity in the same way as F. Further investigation on this film: Al- $\text{MoO}_3$ - $\text{KClO}_4$  and silicone binder included a carbon fiber reinforcement fabric to improve the structural integrity of the film. The inclusion of carbon fiber reinforcement decreased the flame speed by 30% but maintained stable and steady energy propagation. The strength of the films were tested and the non-reinforced film failed upon initial loading of approximately 2.27 kg while the reinforced film maintained a load of 72.3 kg (**Fig. 8**). While this method of synthesis allows manufacture of a flexible free-standing energetic film, the composition and rheology of the mixed slurry have potential as an extrusion cast energetic for additive manufacturing of energetic materials.



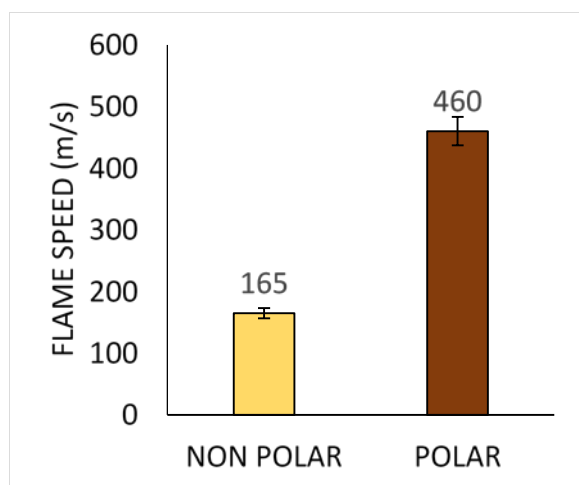
**Figure 7.** Photo graph of flexible free standing energetic film. A. Thermal instabilities illustrated by unsteady energy propagation from film containing 0 wt%  $\text{KClO}_4$  concentration. B. Steady energy propagation observed for films with 30 wt %  $\text{KClO}_4$  concentration.



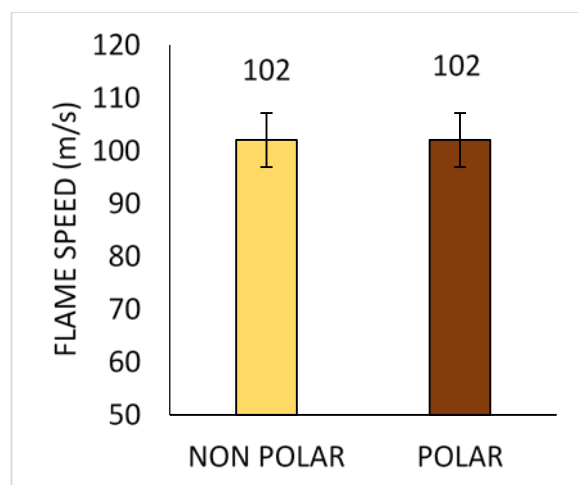
	Maximum Load (Kg)	$\sigma_{\max}$ (kPa)
Non Reinforced Film	2.27	861.84
Reinforced Film	72.3	168420.0

**Figure 8.** Image of mechanical testing on the fiber reinforced energetic thin film compared to the non-reinforced film. The maximum load and stress are reported in the table.

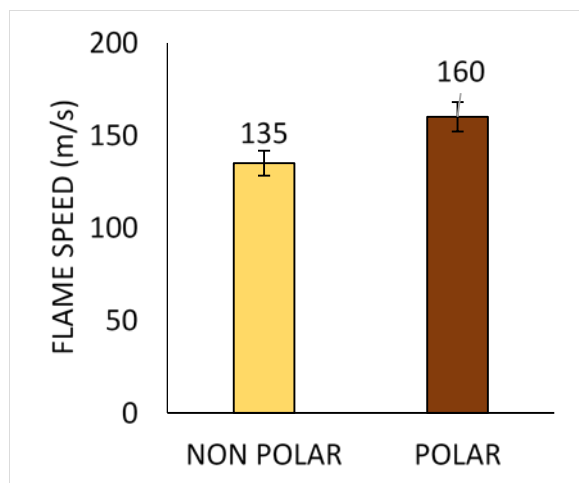
We extended the study shown in **Figs. 1-3** to analyze the effect of surface hydration on reactivity of non-halogen containing oxidizers. Here we compared reactivity of  $\text{Al} + \text{PTFE}$  and  $\text{Al} + \text{I}_2\text{O}_5$  to  $\text{Al} + \text{CuO}$  and  $\text{Al} + \text{MoO}_3$ . Flame speed results are shown in **Fig. 9**. The most interesting finding is in **Fig. 9C** – some metal oxides show increased flame speeds when processed in polar solvents. The hydration layer has an effect on energy propagation for reactions that extend beyond just the halogen species. We investigated the chemistry of  $\text{CuO}$  compared with  $\text{MoO}_3$  and learned that  $\text{MoO}_3$  hydrates more than  $\text{CuO}$  – which resists hydration. The added water in the  $\text{Al} + \text{MoO}_3$  actually aids combustion. This was also shown with CHEETAH modeling including small water concentration within reactants. Simulations show slight increases in flame temperature and heat of combustion.



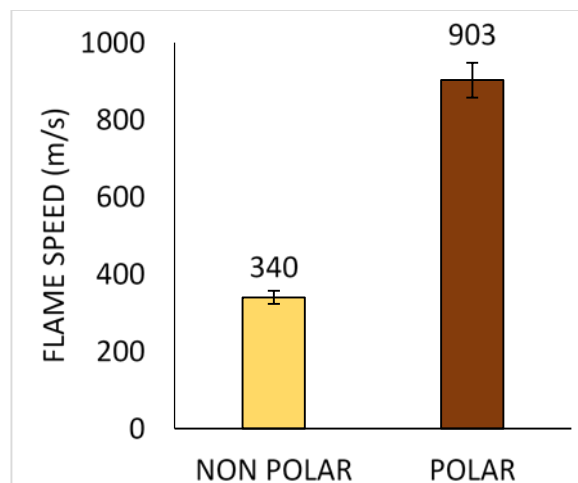
a. Al + PTFE



b. Al + CuO



c. Al + MoO<sub>3</sub>

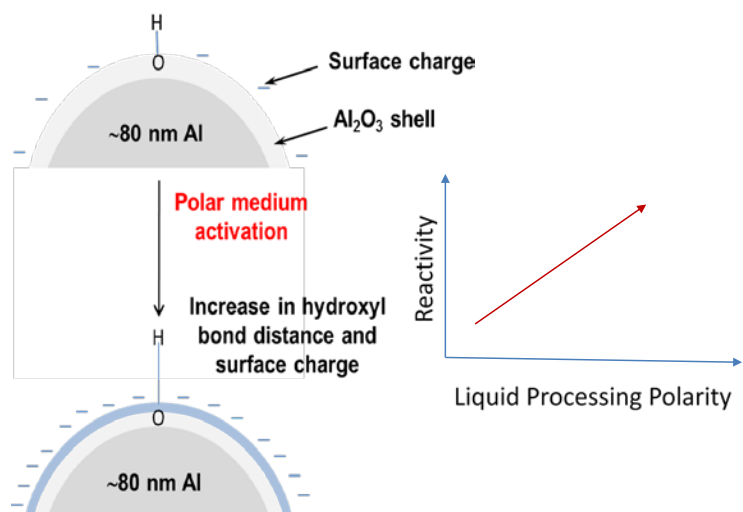


d. Al + I<sub>2</sub>O<sub>5</sub>

**Figure 9.** Flame speed results for a. Al + PTFE; b. Al + CuO; c. Al + MoO<sub>3</sub>; and, d. Al + I<sub>2</sub>O<sub>5</sub>. The error bars give the 95 % confidence limits based on three tests and the average flame speed is reported above each bar. There is a big difference in the influence of Al hydration on reactivity for halogen oxides (i.e., PTFE and I<sub>2</sub>O<sub>5</sub>); no difference for CuO but a slight increase for MoO<sub>3</sub>. The metal oxide, MoO<sub>3</sub> more readily hydrates than CuO such that there is more water species in the Al + MoO<sub>3</sub> that promotes greater reactivity based on CHEETAH simulations.

Density functional theory (DFT) calculations were performed to understand molecular variations on an alumina surface due to exposure to a polar environment. The analysis has strong implications for the reactivity of aluminum (Al) particles passivated by an alumina shell. Recent studies have shown a link between the carrier fluid used for Al powder intermixing and the reactivity of Al with fluorine containing reactive mixtures. Specifically, flame speeds show a threefold increase when polar liquids are used to

intermix aluminum and fluoropolymer powder mixtures. It was hypothesized that the alumina lattice structure could be transformed due to hydrogen bonding forces exerted by the environment that induce modified bond distances and charges and influence reactivity. In this study, the alumina surface was analyzed using DFT calculations and model clusters as isolated systems embedded in polar environments (acetone and water). The conductor-like screening model (COSMO) was used to mimic environmental effects on the alumina surface. Five defect models for specific active –OH sites were investigated in terms of structures and vibrational –OH stretching frequencies. The observed changes of the surface OH sites invoked by the polar environment were compared to the bare surface. The calculations revealed a strong connection between the impact of carrier fluid polarity on the hydrogen bonding forces between the surface OH sites and surrounding species. Changes were observed in the OH characteristic properties such as OH distances (increase), atomic charges (increase), OH stretching frequencies (decrease); and these consequently improve OH surface reactivity (see **Fig. 10**). The difference between medium (acetone) and strong (water) polar environments was minimal in the COSMO approximation.



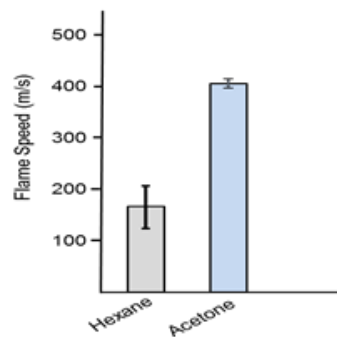
**Figure 10.** Schematic showing the DFT predictions for –OH surface variations due to hydration. Table includes charge data on the surface. Overall exposing the alumina surface to hydration increases bond distances and atomic charges at the surface and these behaviors correlate to increased flame speed (as shown below for Al + PTFE flame speeds following treatment in a polar (acetone) and non-polar (hexane) solvent.

Table 3. Natural atomic charges (*e*) of selected atoms of clusters I–V using the B-P/SVP approach for the isolated cluster (bare surface) and acetone and water as polar environments.

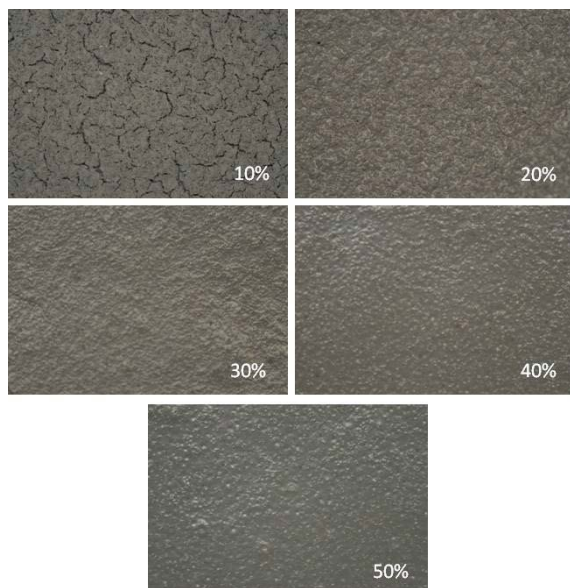
Site	O			H			O-H			Al <sub>i</sub>			Al <sub>o</sub>		
	bare	acetone	water	bare	acetone	water	bare	acetone	water	bare	acetone	water	bare	acetone	water
I	-1.167	-1.181	-1.182	0.509	0.511	0.511	-0.658	-0.670	-0.671	-	-	-	1.990	1.984	1.983
II <sup>a</sup>	-1.226/	-1.229/	-	0.564/	0.561/	0.561	-0.662/	-0.668/	-0.668/	-	-	-	1.998	2.005	2.005
	-1.155	-1.174	1.229/	0.530	0.555	/	-0.625	-0.619	-0.618	-	-	-	-	-	-
			-1.175			0.557									
III	-1.165	-1.184	-1.185	0.553	0.586	0.588	-0.579	-0.598	-0.597	-	-	-	1.930	1.942	1.943
IV	-1.187	-1.191	-1.192	0.536	0.538	0.539	-0.651	-0.653	-0.653	2.087	2.088	2.087	-	-	-
V <sup>b</sup>	-1.232	-1.236	-1.247	0.535	0.533	0.529	-0.697	-0.703	-0.718	2.025	2.031	2.037	2.022	2.019	2.029

<sup>a</sup> the first number for O and H atoms is an average value for two OH sites involved in hydrogen bonds. The second number is for free OH group. Al charges are calculated as an average value over all corresponding Al atoms;

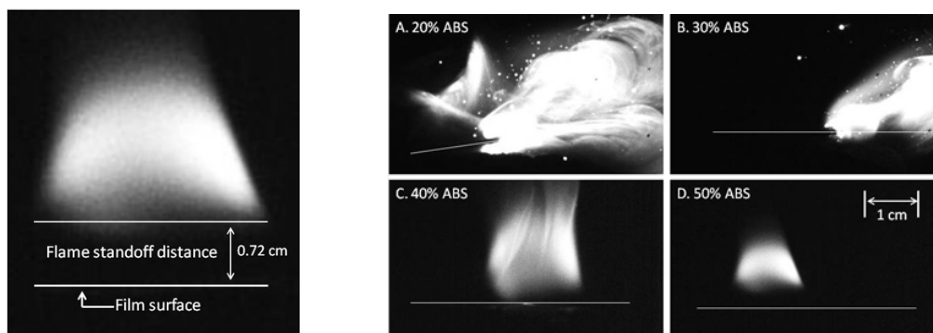
<sup>b</sup> O and H charges calculated as an average value over 3 equivalent sites



Extending the understanding of surface chemistry on aluminum towards synthesis of composites with unique binders has also been explored. In particular we are examining processing and characterization of an energetic material synthesized with a binder that is extensively used in existing additive manufacturing methods. Aluminum (Al), molybdenum trioxide ( $\text{MoO}_3$ ), and potassium perchlorate ( $\text{KClO}_4$ ) are suspended in a solvent-binder system comprised of acetone solvent and acrylonitrile butadiene styrene (ABS) binder. The concentration of ABS is varied from 10 to 50 wt. % and the mass of acetone is correspondingly varied to ensure a slurry with constant volume percent solids. Three-dimensional films are cast with 1 mm thickness for all ABS concentrations tested. Rheological results show that all slurries exhibit non-Newtonian shear thinning behavior for viscosity as a function of shear rate, such that negligible extrudate swell (i.e., die swell) is produced. Investigation into the viscoelastic properties of the slurries revealed them to be highly elastic such that thin sections in the film that cause crack formation can be induced (**Fig. 11**). These results combine to show that 20 wt. % ABS is a minimum threshold for ABS to provide a matrix capable of supporting the energetic materials and the elastic nature of the slurry contributes to crack formation below this threshold. Flame speed characterization showed that at and above 40 wt. % ABS, the volatiles produced from the thermal degradation of the polymer cause burning above the surface of the film excluding the energetic materials from the reaction. Polymer concentration of 20 wt. % (i.e., 80 wt. % energetic material loading) exhibited the highest flame speeds of 1.21 cm/s with an energy density estimated as 5737 kJ/kg. Optimal energetic composites processed using additive manufacturing are achieved if binder concentration can be minimized, as shown here.



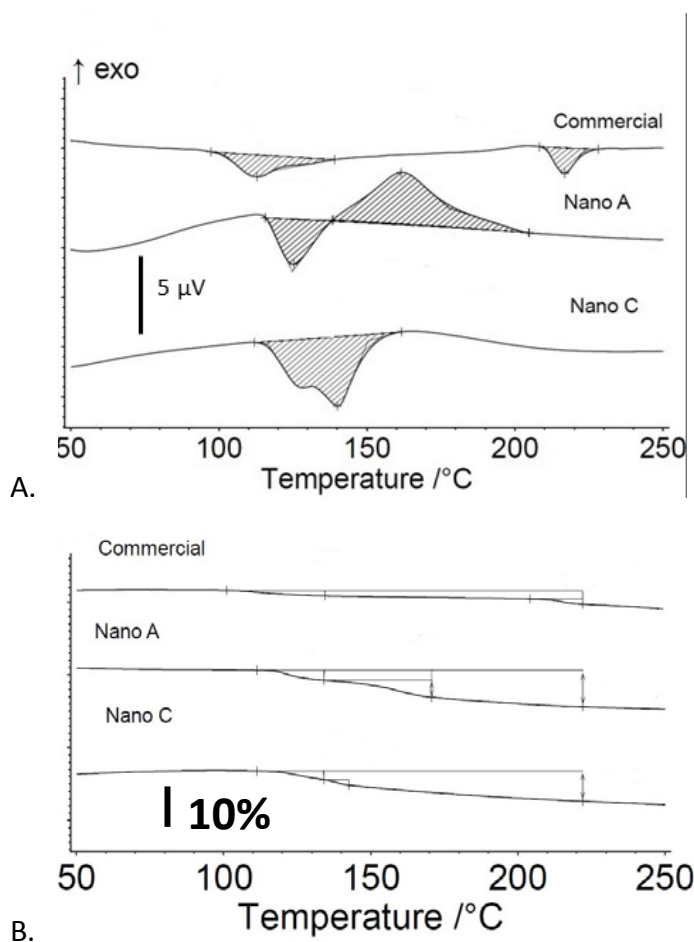
**Figure 11.** Still frame photographs of five ABS concentrations with their corresponding wt. % of ABS indicated in each image. Note crack formations due to viscoelastic effects. **Below Left:** Image for a 50 wt. % ABS film with flame burning, marked by the upper white line, at a standoff distance from the surface of the film, marked by the lower white line. Standoff distance of flame is 0.72 cm. **Below Right:** The flame height is compared to horizontal film position for A. 20 wt. % ABS, B. 30 wt. % ABS, C. 40 wt. % ABS, and D. 50 wt. % ABS. The film position is indicated by the white line and is not horizontal in image A. due to the film lifting during combustion. Scaling is held constant for all images.





Much of our macroscopic energy characterization focuses on flame speed measurements. We have taken the time to present this diagnostic in a more complete sense as many have started to question the functionality of this experiment. Towards this end, we are in the process of publishing a methods article in the *Journal of Visualized Experiments* (which includes a 10 minute movie of the paper). The movie is in production and will enable other researchers to understand the nuances of performing flame speed measurements. This methods article used Al with  $I_4O_9$  as the oxidizer and the complementary DSC work shows signs of pre-ignition reactions that we are resolving further.

Regarding further studies of the pre-ignition reaction with iodine species, we have also isolated a property of the iodine compound that clearly enhances the PIR. In this study amorphous and crystalline  $I_2O_5$  was synthesized specifically for combustion characterization with Al. **Figure 12** clearly shows a dramatic PIR for amorphous  $I_2O_5$  (i.e., labeled Nano A) while the crystalline samples (Nano C and Commercial) do not exhibit as strong behavior.

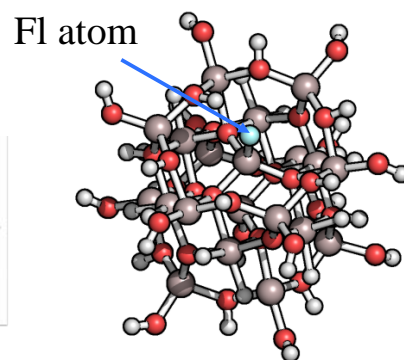
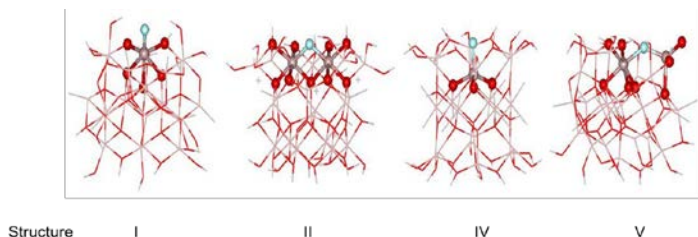


**Figure 12.** A. Heat flow (i.e., DSC plot) of Al mixed with commercial  $I_2O_5$ ; nano A  $I_2O_5$ , and nano C  $I_2O_5$  using isopropanol as the intermixing fluid that is evaporated prior to analysis. B. Corresponding mass loss, starting and ending points for TG were determined using onset and end temperature calculated from DSC Plot and samples were never exposed to > 20 % RH. Nano A clearly shows a strong PIR reaction not seen with the crystalline samples.



As shown above, for fluorination reactions, hydroxyl bonding, inherent on alumina, is a key indicator of the onset and magnitude of the PIR. Our experimental results complement density functional theory (DFT) calculations that examine surface chemistry between alumina and four fluorinated, fragmented molecules representing species from decomposing fluoropolymers: F<sup>-</sup>, HF, CH<sub>3</sub>F, and CF<sub>4</sub> (**Fig. 13**). Four defect models for specific active –OH sites were investigated including two terminal hydroxyl groups and two hydroxyl bridge groups. Reactions involving terminal bonds produce more energy than bridge bonds (**Fig. 14**). This result implies that by enhancing terminal bond coverage, we can optimize energy generation. Surface exothermic reactions between terminal –OH bonds and fluorinated species produce energy in decreasing order with the following reactant species: CF<sub>4</sub> > HF > CH<sub>3</sub>F (**Fig. 14**). Additionally, experiments were performed on aluminum powders using thermal equilibrium analysis techniques that complement the calculations. Consistently, the experimental results show a linear relationship between surface exothermic reactions and the main fluorination reaction for Al powders (**Fig. 15**). These results suggest that polar carrier fluids may provide more terminal bond coverage and this will be investigated further in the future. These results connect molecular level reaction kinetics to macroscopic measurements of surface energy and show that optimizing energy available in surface reactions linearly correlates to maximizing energy in the main reaction (at least under equilibrium conditions). We will extend this study to higher heating rate reaction behaviors.

#### ❖ Four types of –OH sites were studied under fluorination

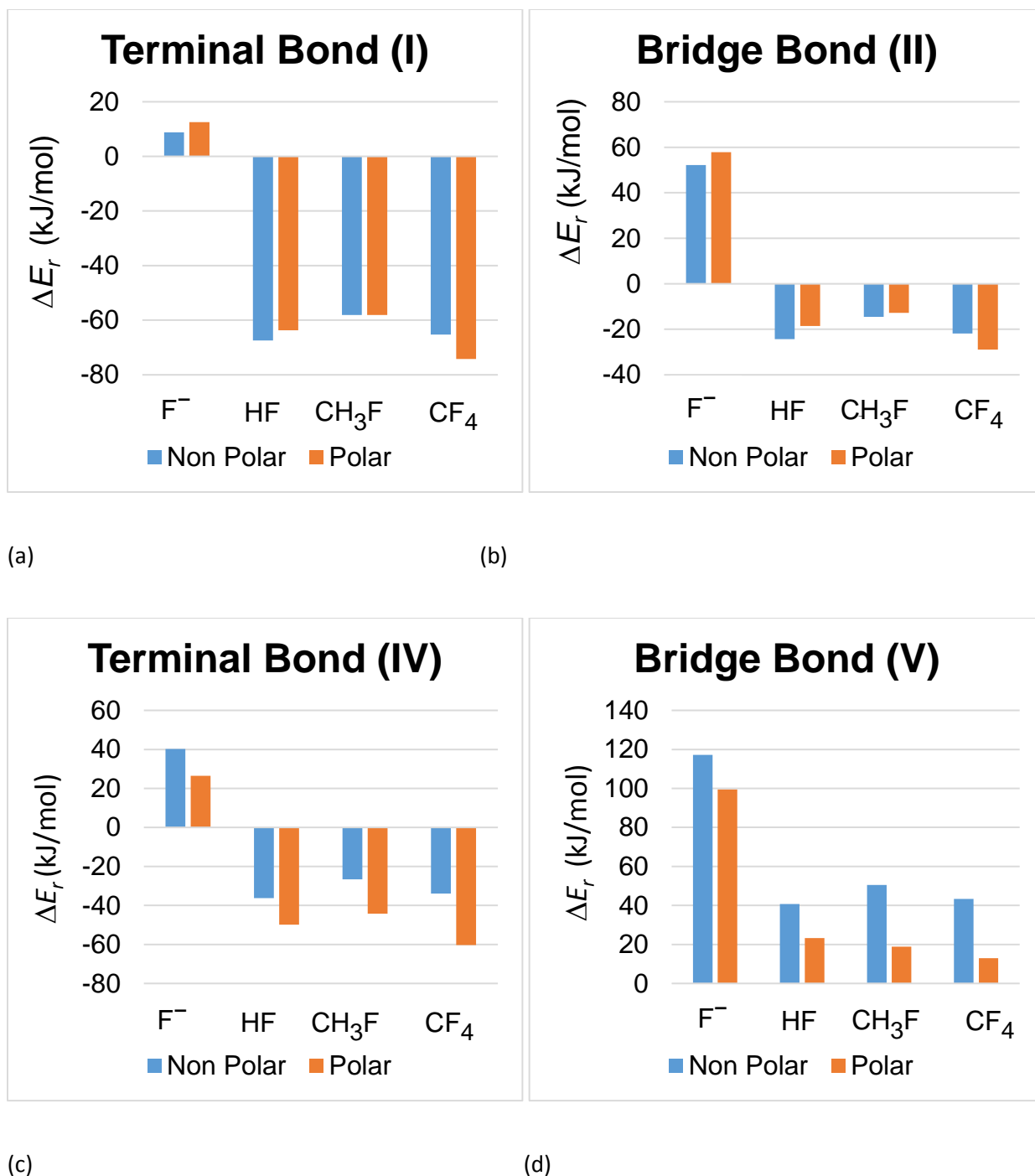


Al<sub>2</sub>O<sub>3</sub> cluster

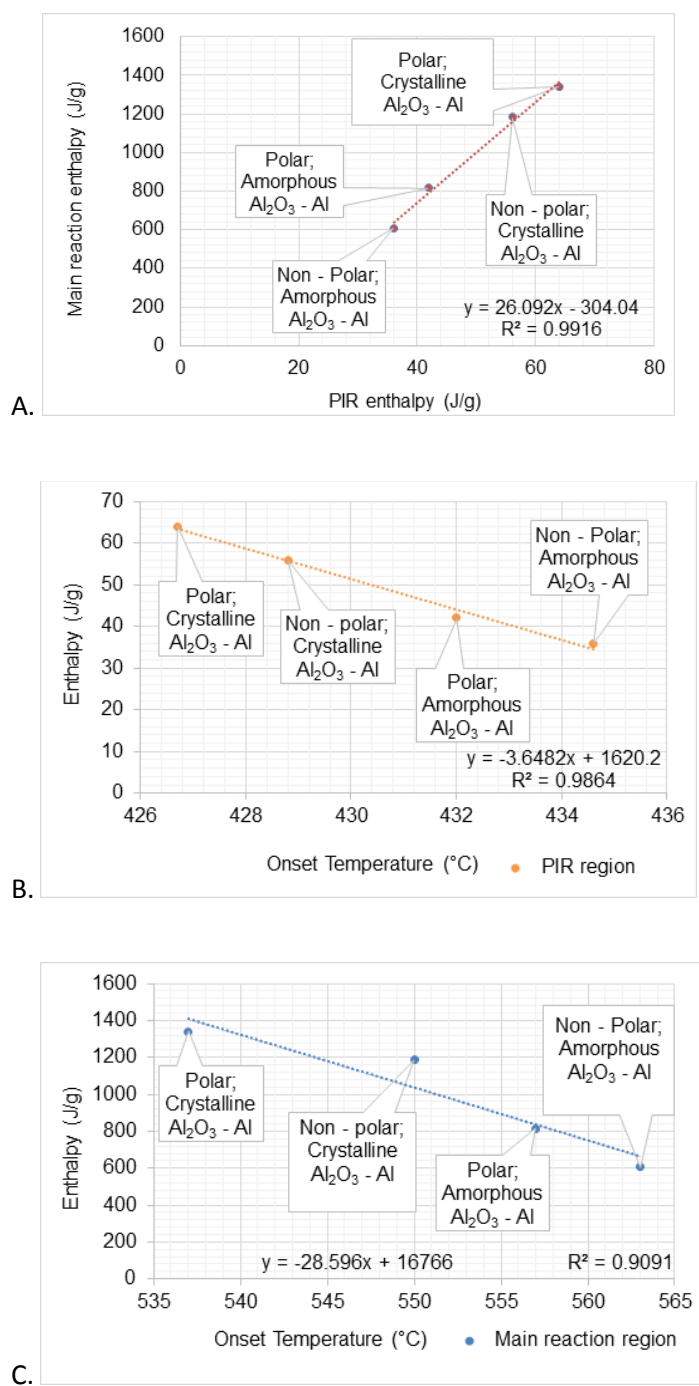
#### ❖ Four elementary reactions were studied

- $\text{Al}_2\text{O}_3\text{-OH} + \text{F}^- \rightarrow \text{Al}_2\text{O}_3\text{-F} + \text{OH}^-$
- $\text{Al}_2\text{O}_3\text{-OH} + \text{HF} \rightarrow \text{Al}_2\text{O}_3\text{-F} + \text{H}_2\text{O}$
- $\text{Al}_2\text{O}_3\text{-OH} + \text{CH}_3\text{F} \rightarrow \text{Al}_2\text{O}_3\text{-F} + \text{CH}_3\text{OH}$
- $\text{Al}_2\text{O}_3\text{-OH} + \text{CF}_4 \rightarrow \text{Al}_2\text{O}_3\text{-F} + \text{CF}_3\text{OH}$

**Figure 13.** Structures of four –OH cluster models. Reaction sites are in a ball-and-stick mode: oxygen atoms in red, fluorine atoms in light blue, and aluminum atoms in tan color. Four elementary reactions were also analyzed based on literature predictions of likely elementary reactions.

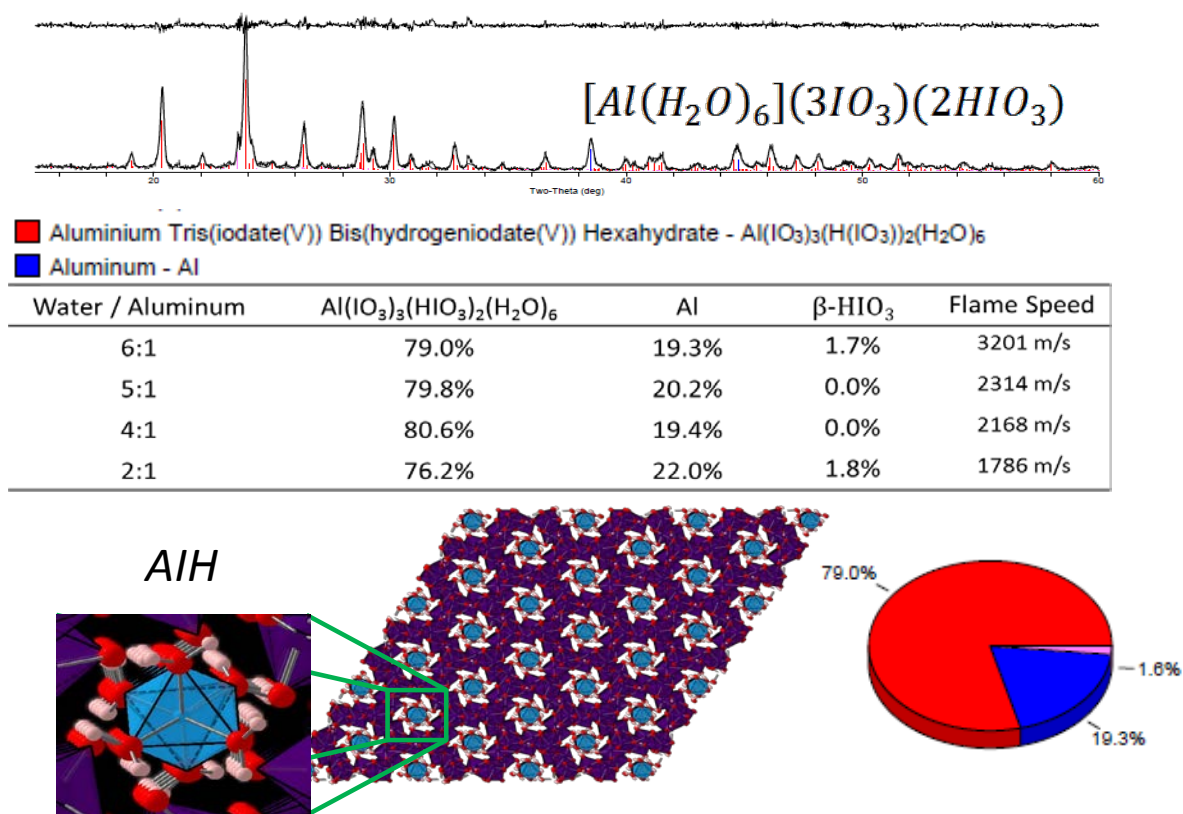


**Figure 14.** Calculated reaction energy ( $\Delta E_r$ , kJ/mol) for (a) hydroxyl octahedral terminal coordination,  $\text{Al}_\text{O}-\text{OH}$  (Site I); (b) hydroxyl octahedral bridging coordination,  $\text{Al}_\text{O}-\text{OH}-\text{Al}_\text{O}$  (Site II), (c) hydroxyl tetrahedral terminal coordination,  $\text{Al}_\text{T}-\text{OH}$  (Site IV), (d) hydroxyl bridging OH linked to one Al in octahedral and one Al in tetrahedral coordination,  $\text{Al}_\text{O}-\text{OH}-\text{Al}_\text{T}$  (Site V). Sites are also shown in **Fig. 13**. Exothermic energy is down (negative).

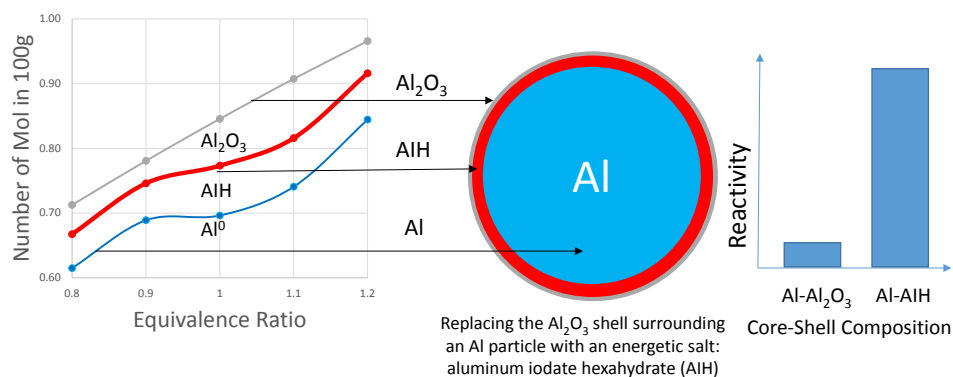


**Figure 15.** A. Main reaction enthalpy as a function of Pre-Ignition Reaction (PIR). B. The PIR enthalpy as a function of onset temperature for reaction; and C. Main reaction enthalpy as a function of onset temperature for reaction. All data measured using DSC. Data points are labeled according to the carrier fluid polarity (i.e., polar or nonpolar) and according to the shell structure (amorphous or crystalline).

Iodine reactions with the alumina shell surface have also been investigated. A crystalline aluminum iodate acid salt has been synthesized from aluminum particles dissolved in iodic acid solution. The precipitate from solution is aluminum iodate hexahydrate (AIH)  $[\text{Al}(\text{H}_2\text{O})_6][\text{IO}_3]_3(\text{HIO}_3)_2$ , as confirmed by X-ray diffraction (XRD) analysis (**Fig. 16**). The method of synthesis first dissolves iodine oxide in water, creating an  $\text{IO}_3^-$  solution with  $\text{pH} < 0.2$ . Aluminum nanoparticles are added to the  $\text{IO}_3^-$  solution and AIH crystals precipitate. The bulk density of the crystalline AIH and Al composite is dependent on the initial water to aluminum concentration ratio during synthesis. Reactivity is characterized in terms of flame speed with measurements as high as 3200 m/s for AIH + Al composite with a calculated density of 3.43 g/cc (**Fig. 16**). These kinetics are shown to approach those of organic molecular explosives. We have learned that surface reactions replace the  $\text{Al}_2\text{O}_3$  passivation layer with AIH (**Fig. 17**). An AIH passivation shell surrounding the Al core particle is a more reactive composite structure than  $\text{Al}_2\text{O}_3$  passivation around Al which facilitates increased reaction rates. The main reaction mechanism that replaces the  $\text{Al}_2\text{O}_3$  passivation layer on Al nano-particles with an energetic AIH salt is pH dependent and is controlled by electrostatic forces that occur between the  $\text{Al}_2\text{O}_3$  passivation layer and free hydrogen atoms ( $\text{H}^+$ ) in solution. When Al particles are added to highly acidic solutions, free  $\text{H}^+$  polarize the Al-O bonds in  $\text{Al}_2\text{O}_3$ , resulting in the formation of  $\text{H}_2\text{O}$  and free  $\text{Al}^{3+}$  cations that complexed by water molecules and exist as  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in aqueous solutions. The concentration of AIH is limited by the amount of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  that forms from the polarization reaction between free  $\text{H}^+$  and the initial  $\text{Al}_2\text{O}_3$  concentration (see **Fig. 17**). The proposed mechanism describes a stoichiometric reaction, but deviations from the stoichiometric reaction are expected with varying equivalence ratios (ER). The polarization mechanism is confirmed by measuring deviations in concentration of final AIH mixtures as a function of ER. A salt formation theory dependent on pH and pKa is used to demonstrate how the final AIH concentrations can be estimated at ER that are not stoichiometric.



**Figure 16.** Top: XRD data for AlH/Al/HIO<sub>3</sub> composite and table includes flame speed measurements as a function of the water to aluminum ratio in the synthesis method. Note pie graph included to better illustrate concentrations of each species detected. Pink section of pie graph is HIO<sub>3</sub>. Bottom: Polyhedral view of the crystal structure of AlH. Iodine is purple, aluminum is blue, hydrogen is pink and oxygen is red. The box on the left is a zoomed-in view of the pore space within the iodate framework that contains the  $Al(H_2O)_6^{3+}$  cation.



**Figure 17.** AlH replacement of  $Al_2O_3$  passivation layer. All lines represent the moles of Al in 100 grams of mixture via XRD analysis.

A variety of ancillary studies have been reported below that complement the above efforts. These studies develop mathematical percolation models relevant to particulate composites; develop diagnostics that analyze or characterize aluminum particles and their reactivity; or, examine additives to tailor

reactivity (e.g., such as indium as a metallic binder and polymers such as ABS for 3D printing, urea for controlling porosity, and allotropes of carbon to adjust thermal properties).

Below are some photographs of our team and collaborators that contributed toward the summary of work described above.



Renita, Michael, Brian Fuchs (ARDEC), Michelle, Kevin, Lee



Michael, Kevin, Michael, Renita, Jesse Sabatini (ARL), Dylan, Lee, Ryan, Richa



Connor, Michael, Kevin, Dylan, Michelle, Lee, Kelsea, Richa, Renita, Phoebe, Michael (June 2017)